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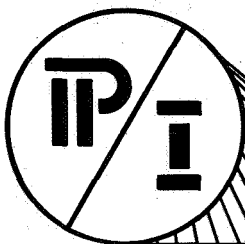
THE MONK CODE

PIFR-119

USER'S MANUAL

February 15, 1969

Final Report to
NASA Manned Spacecraft Center
Meteoroid Sciences Branch
Houston, Texas
Contract NAS 9-8030



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THE MONK CODE (VERSION 1) USER'S MANUAL

SECTION I

INTRODUCTION

The MONK, developed by PI under the joint sponsorship of DASA and NASA is a code for generating equation of state data. The input consists of

1. required input parameters, such as atomic number, S.T.P. volume.
2. required input tables, such as the thermal coefficient of volume expansion versus temperature.
3. optional input data sets that may include parameters such as melting point, boiling point, a known sublimation point V_{SUBL} , T_{SUBL} and others.
4. a list of input E, V for which P and T will be computed for output.

This last input feature accounts for more than half of the code complexity than would have been present had E and T been chosen for input. The E, V input choice has the virtue that (with minor recoding of MONK MAIN) the code can be adapted to a mode that outputs Hugoniot point corresponding to a V input list, and constructs release adiabats from each Hugoniot point. This capability, and others, would not exist had the more simple V, T input method been used.

A disadvantage occurs in the fact that some V, E input pairs may not be processed by the code because of thermodynamical inconsistency. For example, EZ is inputted to be the internal energy of the solid at $P = 1$ atmos, $T = 0$, and thus establishes the energy reference level. Then certain pairs of E,V may be thermodynamically consistent with a negative temperature. In this case, the thermodynamic models are abandoned and a message appears.

In all cases, the output is P, T and NG, the pressure, temperature and mole fraction of gas present in the cases where some or all of the solid has vaporized.

The code is structured and compartmentalized to facilitate adaptation to different models, different input/output formats and different options.

As mentioned earlier, the code requires tables of compressibility, specific heat and other quantities versus temperature. This suggests that the equation of state must be known before the correct input data can be established. This is not the case. It is important to view MONK in the correct perspective to utilize its property as a useful tool.

The proper view is to regard questionable (required) input data as "trial" data to be adjusted and refined by employing the MONK code in a parametric investigation to optimize the fit of the output data to "known" regions of the equation of state. By "known" is meant (1) experimental data or (2) theoretical data obtained for regions in which theory is thought to be accurate. The extrapolation or interpolation

into the unknown regions according to the MONK physical models is then enormously better than can be done by curve fitting or by "eye." For example, the existing Version 1 of MONK treats the simultaneous existence of gaseous and condensed states in thermodynamical equilibrium, a situation that cannot be interpolated or extrapolated from states of pure phase.

MONK, Version 1, contains physical models appropriate for a condensed phase (solid or liquid), a neutral vapor phase, and mixed vapor and condensed phases. This version has a variety of input options, according to the data that are available for a particular substance. Indeed, the methods of input are large enough that not all of the combinations have been exercised at this time, and it is conceivable that not all of the logical bugs have been eliminated. If any logical bugs are discovered, they will be corrected and appropriate addenda will be supplied to all users to correct the user's manual.

Physics International feels that the optimum utilization of this code will first require a period of learning by trial and error. It is envisioned that Version 2 will be similar to Version 1 except that the expression for the nuclear contribution to the pressure will be written as an expansion in $(\frac{V_o - V}{V})$ rather than $(\frac{V_o - V}{V_o})$. This new version will be more suitable at high compressions and will be such that the coefficients are more proper for fitting to Hugoniot data, rather than the present version that requires input lists of compressibility, X and $(\frac{dX}{dP})_T$ and thermal coefficient of volume expansion, all versus temperature.

Section 2 will discuss the physical models used in MONK, Version 1.

Section 3 will discuss the phase line and the determination of solid-gas molar fractions.

Section 4 will list and discuss the input parameters and options.

Section 5 will provide a concordance of all common variables.

Section 6 will list all subroutines and FORTRAN functions and give a brief description.

Section 7 provides five flow charts of particular interest.

A particularly elegant feature of MONK is the "built in" flow chart and diagnostic logic. The programmer should note the method whereby the first input data card can be punched to trigger the "Tracem" logic for any or all subroutines. This is a splendid method of localizing and debugging new models and options, and provides a "flow chart" that adapts itself to changes in the code.

Code decks and listing are provided along with a test input deck and output printouts. The trial material is "aluminum" although no particular care has been taken to optimize the input parameters. Therefore, the aluminum output data should not be regarded as accurate. The purpose was to demonstrate that the physical models of the code were being activated and used correctly.

SECTION II

PHYSICAL MODEL OF MONK, VERSION 1

This present version treats a neutral vapor phase, a condensed phase (which we will call solid), and mixtures of the two. Units for P, V, E and T are atmospheres, cc/mole, atmos-cc/mole and degrees Kelvin.

2.1 The Solid Phase

The solid phase is constructed from a sum of nuclear contributions and electronic contributions.

2.1.1 The nuclear contribution to the solid pressure

$$P_N(V,T) = P_O(T) + P_1(T) * (1 - \frac{V}{V_O}) + P_2(T) * (1 - \frac{V}{V_O})^2$$

where V/V_O is the relative volume with respect to the reference volume, V_O , usually defined at S.T.P. or at $P = 1$ atmos, $T = \text{zero } ^\circ\text{K}$. This expressions obviously is not realistic for small or large values of V/V_O . For metals and minerals, the range of applicability of P_N is probably $.7 \lesssim V/V_O \lesssim 1.4$, corresponding to pressure of a few megabars or hundreds of kilobars at the low volume extreme to the solid-gas transition limit ($\frac{V_{\text{CRIT}}}{V_O} \lesssim 1.4$) at the other extreme. The gas phase description will then take over completely for $V > V_{\text{CRIT}}$.

The inverse expansion of $P_N(V,T)$ is

$$V(P,T) = V_O [1 + a_O(T)] - a_1(T)P + a_2(T)P^2$$

where

$$P_o = a_o/a_1$$

$$P_1 = [1 + 2a_o a_2/a_1^2]/a_1$$

$$P_2 = a_2/a_1^3$$

The a 's in turn are related to the thermal coefficient of volume expansion $\alpha(T) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P=1 \text{ atm}}$ (which in turn is three times the thermal coefficient of linear expansion). The relationships for a_o are:

$$\ln[1 + a_o(T)] = \int_0^T \alpha(T) dt$$

$$a_o(T) = \exp \left[\int_0^T \alpha(T) dt \right] - 1$$

$$\alpha(T) = \frac{1}{1+a_o} \frac{da_o}{dT} \approx \frac{da_o}{dT}$$

Thus, $\alpha(T)$ is required as an input table. The relationships for a_1 and a_2 require the compressibility

$$\chi(T) = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

and

$$\chi'(T) = \left(\frac{\partial \chi}{\partial P} \right)_T$$

The desired relationships are then

$$a_1 = (1 + a_o)\chi$$

$$a_2 = (1 + a_o)\chi'/2$$

Thus the nuclear contribution to solid pressure $P_N(V,T)$ requires an input of V_o and three input lists, $\alpha(T)$, $\chi(T)$ and $\chi'(T)$, labeled ALPHA, CHI and CHIP in the code.

2.1.2 The nuclear contribution to the solid internal energy

$$dE_N(V,T) = \left(\frac{\partial E_N}{\partial V}\right)_T dV + \left(\frac{\partial E_N}{\partial T}\right)_V dT$$

where

$$\left(\frac{\partial E_N}{\partial V}\right)_T = T\left(\frac{\partial P_N}{\partial T}\right)_V - P_N$$

$$\left(\frac{\partial E_N}{\partial T}\right)_V = C_V^O(T), \text{ the specific heat}$$

$$E_N(V,T) = \int_{V_o, T_o}^{V, T} dE_N = E_z + \int_0^T C_V^O(T) dT$$

$$-V_o \left[T \frac{dP_o}{dT} - P_o \right] \left(\frac{V_o - V}{V_o} \right)$$

$$- \frac{V_o}{2} \left[T \frac{dP_1}{dT} - P_1 \right] \left(\frac{V_o - V}{V_o} \right)^2$$

$$- \frac{V_o}{3} \left[T \frac{dP_2}{dT} - P_2 \right] \left(\frac{V_o - V}{V_o} \right)^3$$

The terms

$$V_0 \left[T \frac{dP_0}{dT} - P_0 \right]; \quad \frac{V_0}{2} \left[T \frac{dP_1}{dT} - P_1 \right]; \quad \frac{V_0}{3} \left[T \frac{dP_2}{dT} - P_2 \right]$$

are constructed in MONK53 (subroutine MONKIO) and are labeled E0, E1 and E2. The integration of C^0_V requires an input list of nuclear specific heat labeled CVO. The integration is performed in MONK11 (function INTGRL) and is called by MONK53 which labels this quantity INCVO. MONK17 (function EN) completes the sum of terms and adds in the input quantity E_z , which is the internal energy/mole of the substance in its reference state V_0 (usually taken at $P = 1$ atmos and $T = 0$).

2.1.3 The nuclear contribution to the entropy of the solid

$$S_N(V,T) = \int_0^T \left(\frac{C_V^0}{T} \right) dT - V_0 \left[\left(\frac{dP_0}{dT} \right) \left(\frac{V_0 - V}{V_0} \right) + \frac{1}{2} \left(\frac{dP_1}{dT} \right) \left(\frac{V_0 - V}{V_0} \right)^2 + \frac{1}{3} \left(\frac{dP_2}{dT} \right) \left(\frac{V_0 - V}{V_0} \right)^3 \right]$$

C_{V0}/T is called CVDT in MONK and is integrated by the function INTGRL called in MONKIO. The sum of terms is then done by MONK30 (function SN).

2.1.4 The electronic contribution to the solid pressure

$$P_E(V,T) = \frac{(LR)^2}{Vg\beta} \text{LOG COSH} \left(\frac{g\beta T}{LR} \right)$$

where

z is input atomic number

$R =$ gas constant = 82.057

$\chi_0 = 1./[1.1605 \times 10^4 \times z^{4/3}]$

$\chi = [0.85 \times T \times \chi_0]^{.59}$

$$LR = z \times R \times \chi / (1 + \chi)$$

$$g = [\text{electronic "Gruneisen"}]^{-1} = \frac{1}{2} = \text{function } LG(VT) = \text{MONK14 function}$$

$$\beta = \text{electron contribution to specific heat} = \text{function } BETA(V,T)$$

$$= \text{MONK13 function} = BETA0 \times \sqrt{V/V_0} \quad \text{where } BETA0 \text{ is input electron specific heat at reference volume, } V_0.$$

2.1.5 The electron contribution to the internal energy of the solid assumes that $g = 2/3$.

$$E_E(V,T) = \frac{9}{4} \frac{(LR)^2}{\beta} \text{LOG COSH} \left(\frac{2\beta T}{3LR} \right)$$

where symbols are defined in 2.2.1

2.1.6 Electron contribution to the entropy of the solid

$$SE(V,T) = \int_0^T \left(\frac{C_V}{T} \right)_{V_0} dT + \int_{V_0}^V \frac{Re}{V} dV, \quad \text{where}$$

$$\begin{aligned} \frac{C_V}{T} = & \frac{2g}{T} (LR) \left[\frac{3LR}{2\beta T} \right] \text{LOG COSH} \left[\frac{2\beta T}{3LR} \right] \\ & + \frac{3}{2T} (1-g) LR \text{TANH} \left[\frac{2\beta T}{3LR} \right] \end{aligned}$$

$$\begin{aligned} \frac{Re}{V} = & \frac{2g}{V} (LR) \left[\frac{LR}{g\beta T} \right] \text{LOG COSH} \left[\frac{g\beta T}{LR} \right] \\ & + \frac{(1-g)}{V} LR \text{TANH} \left[\frac{g\beta T}{LR} \right] \end{aligned}$$

where

$$\chi = (T * \chi_0)^{0.59}$$

$$\chi_1 = 0.85 * \chi$$

$$Y = 0.59 / (1 + .05\chi)$$

$$LR = z * R * \chi_1 / [T * (1 + \chi_1)]$$

$$\beta = \text{BETA}(V_0, T)$$

All other symbols and functions have been defined earlier.

CV/T is computed by MONK31 (function $CVT(T)$).

R_e/V is computed by MONK32 [function $REV(V)$]. The integrations are performed by function $INTGRL$. Finally, MONK33 [function $SE(V, T)$] sums the two integrals to obtain the electronic contribution to the solid entropy, $SE(V, T)$.

2.1.7 The total solid pressure

$$P_S = P_N + P_E \quad \text{MONK16 [function } PS(V, T)]$$

2.1.8 The total solid internal energy

$$E_S = E_N + E_E \quad \text{MONK 19 [function } ES(V, T)]$$

2.1.9 The total solid entropy

$$SS = S_N + S_E \quad \text{MONK 34 [function SS(V,T)]}$$

2.1.10 The Helmholtz free energy of the solid

$$FS = E_S - TS_S \quad \text{MONK 37 (function FS)}$$

2.2 The Gas Phase

2.2.1 The gas pressure

$$PG(V,T) = \frac{RT}{V} \left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \frac{E(T)}{V^4} + \dots \right]$$

is the virial equation of state, with the virial coefficients corresponding to B, C, etc. The reduced virial coefficient $B^*(T^*) = B(T)/B_0$ and the derivative

$$B_1^*(T^*) = T^* \left(\frac{dB^*}{dT^*} \right)$$

must be inputed in a list along with the reduced temperature, T^* . For example, see Appendix Table 1-B of Hirshfelder, Curtis and Bird. Twenty-five values of T^* , B^* and B_1^* can be inputed directly for TBASK, BASK and BASK1. The code then constructs

$$T = T^*/(k/\epsilon)$$

from

$$\epsilon/k = EDK = (0.77 \text{ TCRIT} + 1.15 \text{ TBOIL} + 1.92 \text{ TMELT} + .291 \text{ TBOYL})/d$$

where d is the number of non-zero input values in the numerator. Thus the user need only input the values TCRIT, TBOIL, TMELT OR TBOYL for which he has some confidence.

The co-volume BO is also constructed by the code.

$$BO = [2.293 VO + .75 VCRIT + 2.0 VBOIL + 2.3 VMELT] / d$$

where d has the previous correspondence and the previous remarks apply.

The virial coefficients C, D and E are approximated by the geometric corrections of overlapping spherical molecules

$$C = .625 BO^2$$

$$D = .2869 BO^3$$

$$E = .1928 BO^4$$

2.2.2 The gas internal energy

$$\begin{aligned} E_G(v,T) &= E_G^0 - \int_v^{\infty} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv \\ &= E_G^0 - RT \left[\frac{T}{V} \frac{dB}{dT} + \frac{T}{2V^2} \frac{dC}{dT} + \frac{T}{3V^3} \frac{dD}{dT} + \dots \right] \end{aligned}$$

The code constructs

$$E_G^0 = \text{DIFFO} + \frac{3}{2} RT - RT \left[\frac{T}{V} \frac{dB}{dT} + \frac{T}{2V^2} \frac{dC}{dT} + \dots \right]$$

where DIFFO is computed in MONK53 (subroutine MONKIO) as a result of Option 1A, 1B or 1C.

OPTION 1A: Input: LSUB \neq 0, then DIFFO = LSUB

OPTION 1B: A sublimation point is known, temp = HTSUB, vol = HVSUB,

$$\Delta E_{\text{sub}} = \text{HSUB}$$

Input: LSUB = 0, HTSUB \neq 0, HVSUB \neq 0, HSUB \neq 0

Then $\text{DIFFO} = A - EZ - B + \text{HSUB}$

where EZ is input (E_0) of solid at reference conditions.

$$A = \text{ES}(\text{HVSUB}, \text{HTSUB}) = \text{I.E. of solid}$$

$B = \text{EG}(\text{HVSUB}, \text{HTSUB}) = \text{I.E. of gas.}$ (Note that this must be the first time that EG is called, so that DIFFO = 0 at this point.)

OPTION 1C: Same as 1B except that the sublimation pressure HPSUB is known and is included in INPUT and HSUB = sublimation enthalpy.
(Not the same as in Option 1B.)

$$\text{DIFFO} = A - EZ + C + \text{HSUB}$$

where A is as before

but $C = \text{EG}(B, \text{HTSUB})$

with B = gas volume consistent with HPSUB and T SUB

$$= \text{FUNCTION VGBNSR}(\text{HPSUB}, \text{T SUB})$$

$$= \text{MONK 38}$$

The meaning of DIFFO is such that the gas and solid phases have internal energies that are measured from the same zero.

It is desirable to input any known sublimation point HTSUB, HVSUB even if Option 1A is used because these quantities will then be used to sharpen the entropy constant in the gas description.

2.2.3 The Gas Entropy

$$\begin{aligned}
 S_G(V,T) &= S_G^0 - R \ln P + R \ln \left(\frac{PV}{RT} \right) - \int_V^\infty \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \\
 &= S_G^0 + R \ln \left(\frac{V}{RT} \right) - \int_V^\infty \left\{ \frac{R}{V} \left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right) \right. \\
 &\quad \left. + \frac{RT}{V} \left(\frac{1}{V} \frac{dB}{dT} + \frac{1}{V^2} \frac{dC}{dT} + \dots \right) - \frac{R}{V} \right\} dV \\
 &= S_G^0 + R \ln \left(\frac{V}{RT} \right) - R \int_V^\infty \left[\frac{B + T \frac{dB}{dT}}{V^2} + \frac{C + T \frac{dC}{dT}}{V^3} + \dots \right] dV \\
 &= S_G^0 + R \ln \left(\frac{V}{RT} \right) - R \left[\frac{B + T \frac{dB}{dT}}{V} + \frac{C + T \frac{dC}{dT}}{2V^2} + \frac{D + T \frac{dD}{dT}}{3V^3} + \dots \right]
 \end{aligned}$$

The base for gas entropy must be adjusted by S_G^0 to be consistent with the solid entropy. S_G^0 will be a constant in this MONK version because we will exclude the possibility of encountering various complications along the phase line. (The phase line is described in Section III.) These complications can be: (1) different condensed states; for example, different solid crystalline structures or solid and liquid. (2) different molecular shapes or arrangements in the gas. (3) The freezing-in of energy states at low sublimation temperatures. (4) The activation of normally inaccessible energy states at high sublimation temperatures.

Ignoring the above complications, we can evaluate the constant value of S_G^0 if we know (or can estimate) a sublimation point temperature and

volume, T_1 and V_1 . At T_1 and V_1 , the Helmholtz free energy of the solid is $F_s(V_1, T_1)$ (see Section 2.1.9) and is equal to the Helmholtz free energy of the gas, $E_g(V_1, T_1) - T_1 S_g(V_1, T_1)$. Thus,

$$S_g(V_1, T_1) = [E_g(V_1, T_1) - F_s(V_1, T_1)]/T_1$$

or

$$S_g^0 + R \ln\left(\frac{V_1}{RT_1}\right) - R \left[\frac{B + T_1 \frac{dB}{dT}}{V_1} + \frac{C + T_1 \frac{dC}{dT}}{2V_1^2} + \dots \right]$$

$$= [E_g(V_1, T_1) - F_s(V_1, T_1)]/T_1$$

$$= \frac{\text{DIFF0}}{T_1} + \frac{3}{2}R - R \left[\frac{T_1}{V_1} \frac{dB}{dT} + \frac{T_1}{2V_1^2} \frac{dC}{dT} + \frac{T_1}{3V_1^3} \frac{dD}{dT} + \dots \right]$$

or

$$S_g^0 = \frac{\text{DIFF0}}{T_1} + \frac{3}{2}R - R \ln\left(\frac{V_1}{RT_1}\right) - F_s\left(\frac{V_1, T_1}{T_1}\right) + R \left[\frac{B}{V_1} + \frac{C}{2V_1^2} + \frac{D}{3V_1^3} + \dots \right]$$

Thus the gas entropy, $SG(V, T)$, is completely defined and is consistent with the entropy scale of the solid. If HTSUB and HVSUB are read in as non-zeros by MONKIO, they are used for T_1 and V_1 . Otherwise T_1 and V_1 are estimated from EDK and BO (constructed in MONKIO) by:

$$T_1 = \text{EDK}/1.15$$

$$V_1 = \text{BO}/2.0$$

This completes the pure phase physical models that are being used. It is expected that other models will be tried and that some time will pass before final recommendations can be made as to the appropriateness of various models for application to various real materials.

In Version 1, three restrictive assumptions have been made, namely (1) that the gas phase will not exist for $V < V_0$ and (2) that pure gas phase will exist if $V > V_{\text{CRIT}} \leq 1.4$ and (3) the temperature range of validity for the solid and (associated-neutral) gas is $10^{-10} \leq T \leq 23,000$ °K. If an input pair of V, E is such that the range of model validity is exceeded, then a diagnostic message will appear. The most common input that will not be processed is the type where

$$(1) \quad E_{\text{INPUT}} < E(T=0, V_{\text{INPUT}})$$

$$(2) \quad E_{\text{INPUT}} > E(T= 10^5 \text{ °K}, V_{\text{INPUT}})$$

Care must be taken to choose input parameters for the models that are consistent with the desired input range of E and V because the code will not allow thermodynamic inconsistency.

SECTION III

THE PHASE LINE AND PHASE MIXTURES

The present model virial expansion for the neutral gas cannot be expected to be correct in the high compression regime $V/V_0 \lesssim 1$ and in the high temperature region $T \gtrsim 23000$ °K (~ 2 electron volts) for our neutral gas assumption.

Similarly, the solid phase in the present model cannot be expected to be modeled correctly outside of the limits $.5 \lesssim V/V_0 \lesssim 1.4$ because of the expansion in $\frac{V_0 - V}{V_0}$ used in the expressions for the nuclear contributions.

Then the interval $1 \lesssim V/V_0 \lesssim 1.4$ represents the overlap region where the two descriptions (gas and solid) can be simultaneously valid except that pure gas must exist above the critical volume V_{CRIT} .

MONKIO sets up the phase line in the volume interval $1.0 \leq V/V_0 \leq V_{\text{CRIT}}/V_0$ by constructing sublimation volume-temperature arrays $\text{VSUB}(I)$, $\text{TSUB}(I)$ such that the gas and solid description Helmholtz free energies are equal.

$F_g(\text{VSUB}, \text{TSUB}) = E_g - TS_g = F_s(\text{VSUB}, \text{TSUB}) = E_s - TS_s$. This phase line is used to determine whether an input E, V pair is consistent with all solid phase, all gas phase, or a mixture of phases at equilibrium. The following logic is used:

- (1) If $E > E_g(V, \text{TSUB}(V))$ then the input energy is greater than that required to achieve the sublimation temperature $\text{TSUB}(V)$ using the gas model and pure gas is present.

- (2) If $E < E_s(V, T_{\text{SUB}}(V))$ then the input energy is less than that required to heat the solid up to the sublimation temperature, hence pure solid phase is present.
- (3) If $E_s < E < E_g$ then a mixture of phases will occur with $N_G = (E - E_s) / (E_g - E_s)$ being the mole fraction of gas. The molar volume of solid and gas are determined by the equality of Gibbs free energies, which is the same as the equality of gas and solid pressure on the phase line.

SECTION IV

INPUT PARAMETERS AND OPTIONS

CARD NO. 1 (Blank unless diagnostic "trace" option is used.)

TRACEM(I), I = 1,65 (FORMAT 65I1)

Any combination of non-zero punches in (say columns 7, 10,35) will activate the trace logic such that every call to MONK 7, 10, and 35 will be printed out along with diagnostic data and nesting level.

All remaining input cards will have floating point data punched in fields of 16 (of the FORMAT type 5E16.9 or 4E16.9).

CARD NO. 2

Z, MW, VO, EZ, BETAO

No zero allowed, no options available.

Z = atomic number

MW = molecular weight (gm/mole)

VO = reference density of solid (cm^3/mole)

EZ = reference internal energy of solid at $V = V_0$, $T = 0^\circ \text{K}$
(atmos-cc/mole)

BETAO = electronic specific heat coefficient at $V = V_0$ (atmos-cc/mole- $^\circ \text{K}^2$)

CARD NO. 3

VCROP, VCRIT, VBOIL, VMELT

Various options. See Flow Chart No. 4.

VCROP = any non-zero number if VCROP option is used.

VCRIT = critical volume if known (cm^3/mole).

VBOIL = boiling volume (cm^3/mole) at $P = 1$ atmos).

VMELT = melting volume (cm^3/mole) at $P = 1$ atmos).

It is desirable to input at least one of the three (VCRIT, VBOIL or VMELT) if possible so that the code can make a good estimate of the co-volume.

The rules of thumb given next are inferior to an understanding of Flow Chart No. 4 and its ramifications.

If VCRIT is known, then input $VCRIT \neq 0$, $VCROP = 0$.

If TCRIT is known better than VCRIT, then it may be better to input TCRIT (next card) with $VCRIT = VCROP = 0$.

If nothing is known: Try (1) blank card and (2) $VCROP \neq 0$ and compare results against physical intuition.

CARD NO. 4

TBOYL, TCRIT, TBOIL, TMELT

TBOYL = Boyle's Temperature $^{\circ}\text{K}$

TCRIT = Critical temperature $^{\circ}\text{K}$

TBOIL = Boiling temperature $^{\circ}\text{K}$ (at $P=1$ atmos)

TMELT = Melting temperature $^{\circ}\text{K}$ (at $P=1$ atmos).

At least one of the above four must be non-zero so that the code can estimate the scale factor EDK for the reduced temperature T^* .

CARD NO. 5

LSUB, HTSUB, HVSUB, HPSUB, HSUB

Various options. See Flow Chart No. 3.

LSUB = internal energy of sublimation of solid at $T = 0^\circ\text{K}$ and

$V = V_0$ (atmos-cc/mole).

= internal energy of the gas at $T = 0^\circ\text{K}$, $V = \infty$.

HTSUB a known temperature ($^\circ\text{K}$), and volume (cm^3/mole) at any
HVSUB sublimation point.

HPSUB = the pressure of the gas at the above known sublimation
point (atmos).

HSUB = either the energy of sublimation (cm^3/mole) if $HPSUB = 0$,
or the enthalpy of sublimation if $HPSUB \neq 0$.

If LSUB is known, it should be used. In this case $\text{DIFFO} = \text{LSUB}$ and all is well.

Even if LSUB is used, it is desirable to input a known sublimation point volume and temperature, HVSUB and HTSUB so that the zero point entropy of the gas (relative to the solid) will be established with good accuracy.

If LSUB is ignored, then HVSUB, HTSUB and HSUB must be used. If, in addition, HPSUB is used then the meaning of HSUB is changed.

It is desirable to understand Flow Chart No. 3.

CARD NO. 6A

N FORMAT(I10)

N = array length that follows ($2 \leq N \leq 25$)

CARD(S) NO. 6B

TCVO(I), CVO(I), TCVO(I+1), CVO(I+1) FORMAT(4E16.9)

TCVO = temp $^{\circ}\text{K}$

CVO = specific heat at constant volume VO of solid
(atmos-cc/mole- $^{\circ}\text{K}$) at temperature TCVO.

TCVO(1) should = 0

TCVO(N) should = 10^{60}

TYPE 7 cards are stacked together in order of increasing temperature.

The method of CARD NO. 6A and CARD(S) NO. 6B is used to input the next arrays:

CARDS NO. 7 TALPHA(I), ALPHA(I), I = 1, N_1 ($2 \leq N_1 \leq 25$)

CARDS NO. 8 TCHI(I), CHI(I), I = 1, N_2 ($2 \leq N_2 \leq 25$)

CARDS NO. 9 TCHIP(I), CHIP(I), I = 1, N_3 ($2 \leq N_3 \leq 25$)

CARDS NO.10 TBASK(I), BASK(I), I = 1, N_4 ($2 \leq N_4 \leq 25$)

CARDS NO.11 TBASK₁(I), BASK₁(I), I = 1, N_5 ($2 \leq N_5 \leq 25$)

where TALPHA, TCHI, TCHIP correspond to the temperatures associated with the values of ALPHA, CHI and CHIP respectively.

TBASK and TBASK₁ correspond to the reduced temperatures associated with BASK and BASK₁ respectively.

CHI = compressibility - $\frac{1}{V}(\frac{\partial V}{\partial P})_T$ of the solid (atmos⁻¹).

$$\text{CHIP} = \left(\frac{\partial \text{CHI}}{\partial P} \right)_T$$

BASK = reduced second virial coefficient. $B^*(T^*)$ of Hirshfelder, Curtis and Bird for the Lennard-Jones potential, at the reduced temperature T^* .

BASK₁ = $T^* \frac{d \text{BASK}}{dT^*}$ and is given in loc. cit. above.

CARD NO. 12

N FORMAT (I2)

N = number of sets of E,V input matrices that will be processed.

CARD NO. 13.1

IEMAX, IVMAX FORMAT (2I4)

IEMAX = number of E's in first set ($1 \leq \text{IEMAX} \leq 10$)

IVMAX = number of V's in first set ($1 \leq \text{IVMAX} \leq 10$)

CARD NO. 13.2

E(I), I = 1, IEMAX FORMAT(5E16.9)

Input list of energies ($\frac{\text{atmos-cc}}{\text{mole}}$)

CARD NO. 13.3

V(J), J=1, IVMAX FORMAT(5E16.9)

Input list of volumes (cm³/mole)

This completes the first input set. Repeat CARD TYPE 13.1, 13.2, 13.3 for each set of desired input.

The output will be P(I,J), T(I,J), NG(I,J) for every combination of I,J in each set.

SECTION V

CONCORDANCE

UNLABELED COMMON

ALPHA(25)	Thermal coefficient of volume expansion (input list)
CVO(25)	Specific heat at constant volume (input list)
CHI(25)	Compressibility of solid, $\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (input list)
TCHI(25)	Temp. list associated with χ (input list)
ICHI(25)	} Intercept and slope of χ . See MONK 10.
SCHI(25)	
CHIP(25)	$\chi' = \left(\frac{\partial \chi}{\partial P}\right)_T$ (input list)
TCHIP(25)	Temp. list associated with χ' (input list)
ICHIP(25)	} Intercept and slope of χ' . See MONK 10.
SCHIP(25)	
BASK(25)	Reduced second virial coefficient. $B^*(T^*)$ of Hirshfelder, Curtis and Bird for Lennard-Jones pot. (input list).
TBASK(25)	Reduced temp, T^* , assoc. with B^* (input list).
IBASK(25)	} Intercept and slope of B^* . See MONK 10
SBASK(25)	
BASK1(25)	$B_1^* = T^* \frac{dB^*}{dT^*}$ of loc. cit. for BASK (input list).
TBASK1(25)	T^* assoc. with B_1^* (input list)
IBASK1(25)	} Intercept and slope of B_1^* . (See MONK 10)
SBASK1(25)	

UNLABELED COMMON

CVODT(25)	$C^O V/T$
P0(151)	Terms in expansion of nuclear contribution to the solid pressure
P1(151)	
P2(151)	
E0(151)	Terms in the expansion of the nuclear contribution to the solid internal energy
E1(151)	
E2(151)	
BK(151)	$BO * B^*$
BKP(151)	$BO * B_1^*/T$
ICVDT(151)	Integral of $(C^O V/T)dT$ from $T = 0$ to $T = T$
TSUBL(392)	List of sublimation temps.

LABELED COMMONS

COMMON/TEMPCM

TEMP(151)	Internal reference list of temps
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COMMON/PNCOMN

IPO(151)	Intercepts and slopes of P0, P1 and P2. Se MONK 10.
SPO(151)	
IP1(151)	
SP1(151)	
IP2(151)	
SP2(151)	
V0	Reference specific molar volume of solid.

COMMON/BETACM

VO1 Same meaning as VO (Ref. vol.)
BETA0 Elect. specific heat at V = VO
BO co-volume

COMMON/PECOMN

X0 = $1./[Z^{4/3} * 1.1605 \times 10^4]$
Z = Atomic number (input)
R = 82.057 = molar gas constant

COMMON/CNCOMN

V02 = V0
EZ = Internal energy of solid at reference conditions (input)

IINCVO(151) }
SINCVO(151) } Intercept and slope of INCVO.

IE0(151) }
SE0(151) }
IE1(151) } Intercepts and slopes of E0, E1 and E2.
SE1(151) }
IE2(151) }
SE2(151) }

COMMON/PGCOMN

R1 = R

COMMON/DBDTCM

IBKP(151)	}	Intercept and slope of BKP = $B0 * BASK1/T$
SBKP(151)		

COMMON/EGCOMN

DIFFO	Internal energy of Gas at $T=0$
R2	=R

COMMON/SNCOMN

IICVDT(151)	}	Intercepts and slopes of: ICVDT, SP0, SP1 and SP2. See MONK 10.
SICVDT(151)		
ISP0(151)		
SSP0(151)		
ISP1(151)		
SSP1(151)		
ISP2(151)		
SSP2(151)		
VO3	= VO	

COMMON/VGBNSC

VCNT	Number of non-zero TSUBL, VSUBL pairs
VOL(391)	Internal volume array for constructing VSUBL, TSUBL

COMMON/MONKER

MONKGO	ERROR SWITCH
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COMMON/FALPHC

NALPHA Alpha array length (input)
TALPHA(25) Temps. corresponding to ALPHA Array (input)
IALPHA(25) }
SALPHA(25) } Intercepts and slopes of ALPHA Array

COMMON/FCVOCM

NCVO CVO array length (input)
TCVO(25) Temps. corresponding to CVO array (input)
ICVO(25) }
SCVO(25) } Intercepts and slopes of CVO array

COMMON/FCVODC

NCVO1 = NCVO
TCVO1(25) = TCVO
ICVODT(25) }
SCVODT(25) } Intercepts and slopes of CVO/T

COMMON/MONKPC

VCRIT = Critical volume
VCNT1 = VCNT = Index count in TSUBL, VSUBL space
VSUBL(391) = Sublimation volume array
ITSUBL(391) }
STSUBL(391) } Intercept and slope of sublimation temp. array.

COMMON/BMONKC

IBK(151) }
SBK(151) } Intercept and slope of BK = BO * BASK

COMMON/SGZCOM

HV SUB

HT SUB

} A particular sublimation point (volume and temp.)

EDK

Ratio of true temp to reduced temp (ϵ/k)

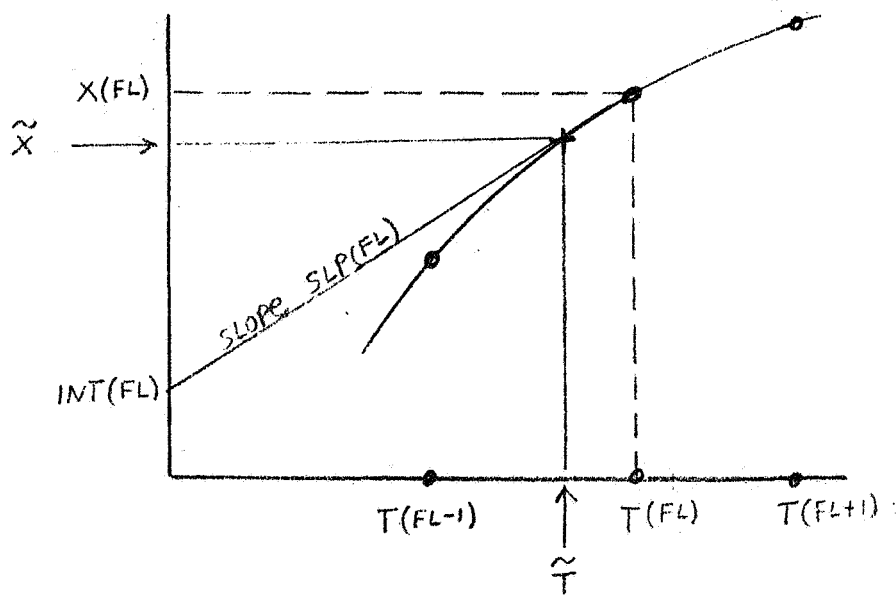
SECTION VI

MONK FORTRAN FUNCTION AND SUBROUTINES, NAMES, AND PRIMARY PURPOSES

MONK NO.	NAME	(ARGUMENT LIST)/PURPOSE
00	MONK	NONE /DRIVER
01	ERRDER	(MONKGO) /ERROR CHECK
02	CHKVLU	(LOVAL, HIVAL, VAL, NAME1, NAME2) /CHECKS A VALUE AGAINST HI AND LO LIMITS
03	CHKFGN	(N, X, Y, NAMEX1, NAMEX2, NAMEY1, NAMEY2, LOVALX, HIVALX, LOVALY, HIVALY) /Checks the N values of X and Y arrays against hi and lo limits
04	CHKN	(N, NAMEX1, NAMEX2, NAMEY1, NAMEY2) /Checks the array length N in the argument of FGEN (MONK 10) against hi and low limits.
05	RITFGN	(N, X, Y, NAMEX1, NAMEX2, NAMEY1, NAMEY2) /Writes out and labels the N values of an X and Y array.
06	FGNSAI	(N, X, Y, INT, SLP) /Given N pairs of values of X, Y arrays, construct slope and intercept arrays, $SLP = dy/dx$, $INT = y - x * SLP$

MONK

NO.	NAME	(ARGUMENT LIST) /PURPOSE
08	ISR	(N,T,X,FL) /Given N values of the array x and a value of T, find index FL such that $X(FL-1) \leq T \leq X(FL)$
09	FFGEN	(X,INT,SLP) /Given a value X, INT and SLP, return value $FFGEN = INT + X * SLP$
10	FGEN	(N, \tilde{T} ,X,INT,SLP) /Given the N values of the X array and the N values of intercept and slope arrays ($SLP = dx/dt$) and given a value of \tilde{T} that does not necessarily have a value corresponding to a member of the array T that was used to set up the arrays $INT(T(I))$ and $SLP(T(I)) = \frac{dx(I)}{dT(I)}$, then a value of \tilde{X} is returned. $FGEN = \tilde{X} = INT(FL(T)) + \tilde{T} * SLP(FL(T))$ Graphically:



MONK

NO.	NAME	(ARGUMENT LIST)	/PURPOSE
-----	------	-----------------	----------

11	INTGRL	(F,AA,BB)	
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/Given a function F(x) with an array of argument x and given lower and upper limits AA = X_{min}, BB = X_{max} where X_{min} and X_{max} need not be array points, then the integral is performed.

$$\text{INTGRL} = \int_{\text{AA}}^{\text{BB}} F(x) dx$$

12	PN	(V,T)	
----	----	-------	--

/nuclear contribution to the pressure of the solid

$$P_N = P_O(T) + P_1(T) \left(\frac{V_O - V}{V_O} \right) + P_2(T) \left(\frac{V_O - V}{V_O} \right)^2$$

Now contained in 16

{	BETA	(V,T)	
---	------	-------	--

/electron specific heat contribution in the solid

$$\text{BETA} = \text{BETAO} * \sqrt{V/V_O}$$

{	LG	(V,T) = 0.5	
---	----	-------------	--

{	PE	(V,T)	
---	----	-------	--

/electron contribution to the solid pressure

$$\text{PE} = \frac{r^2}{\text{VGB}} \log \cosh\left(\frac{\text{GBT}}{r}\right)$$

MONK NO.	NAME	(ARGUMENT LIST) /PURPOSE
16	PS	(V,T) /Total pressure of solid phase $PS = PN + PE$
17	EN	(V,T) /Nuclear contribution to the internal energy of the solid. $EN = E_Z + \int_0^T C_v^0(T) dT - (V_0 - V) \left[T \frac{dP_0}{dT} - P_0 \right] \\ - \frac{(V_0 - V)^2}{2V_0} \left[T \frac{dP_1}{dT} - P_1 \right] \\ - \frac{(V_0 - V)^3}{3V_0^2} \left[T \frac{dP_2}{dT} - P_2 \right]$
18	EE	(V,T) /Electron contribution to the internal energy of the solid. $EE = \frac{q}{4} \frac{n^2}{\beta} \log \cosh \left(\frac{2\beta T}{3n} \right)$
19	ES	(V,T) /Total internal energy of solid phase $ES = EN + EE$
24	PG	(V,T) /Total pressure of gas phase (VIRIAL EXPANSION) $PG = \frac{RT}{V} \left[1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \frac{E}{V^4} \right]$

MONK

NO.	NAME	(ARGUMENT LIST)	PURPOSE
-----	------	-----------------	---------

29	EG	(V,T)	
----	----	-------	--

/Internal energy of gas phase

$$EG = DIFFO + \frac{3}{2} RT - RT \left[\frac{1}{V} \frac{dB}{dT} + \frac{1}{2V^2} \frac{d^2B}{dT^2} + \frac{1}{3V^3} \frac{d^3B}{dT^3} + \dots \right]$$

30	SN	(V,T)	
----	----	-------	--

/Nuclear contribution to the entropy of the solid

$$SN = \int_0^T \frac{C_V^0}{T} dT - V_0 \left[\left(\frac{V_0 - V}{V_0} \right) \frac{dP_0}{dT} + \frac{1}{2} \left(\frac{V_0 - V}{V_0} \right)^2 \frac{d^2P_0}{dT^2} + \frac{1}{3} \left(\frac{V_0 - V}{V_0} \right)^3 \frac{d^3P_0}{dT^3} \right]$$

31	CVT	(T)	
----	-----	-----	--

/Term CV/T that will be used in the evaluation of the electron contribution to the entropy of the solid phase.

$$CVT = \frac{C_V}{T} = \frac{2\gamma r}{T} \left(\frac{3r}{2\beta T} \right) \log \cosh \left(\frac{2\beta T}{3r} \right)$$

32	REV	(V)	
----	-----	-----	--

/Term Re/V that also will be used in the evaluation of the electron contribution to the entropy of the solid phase.

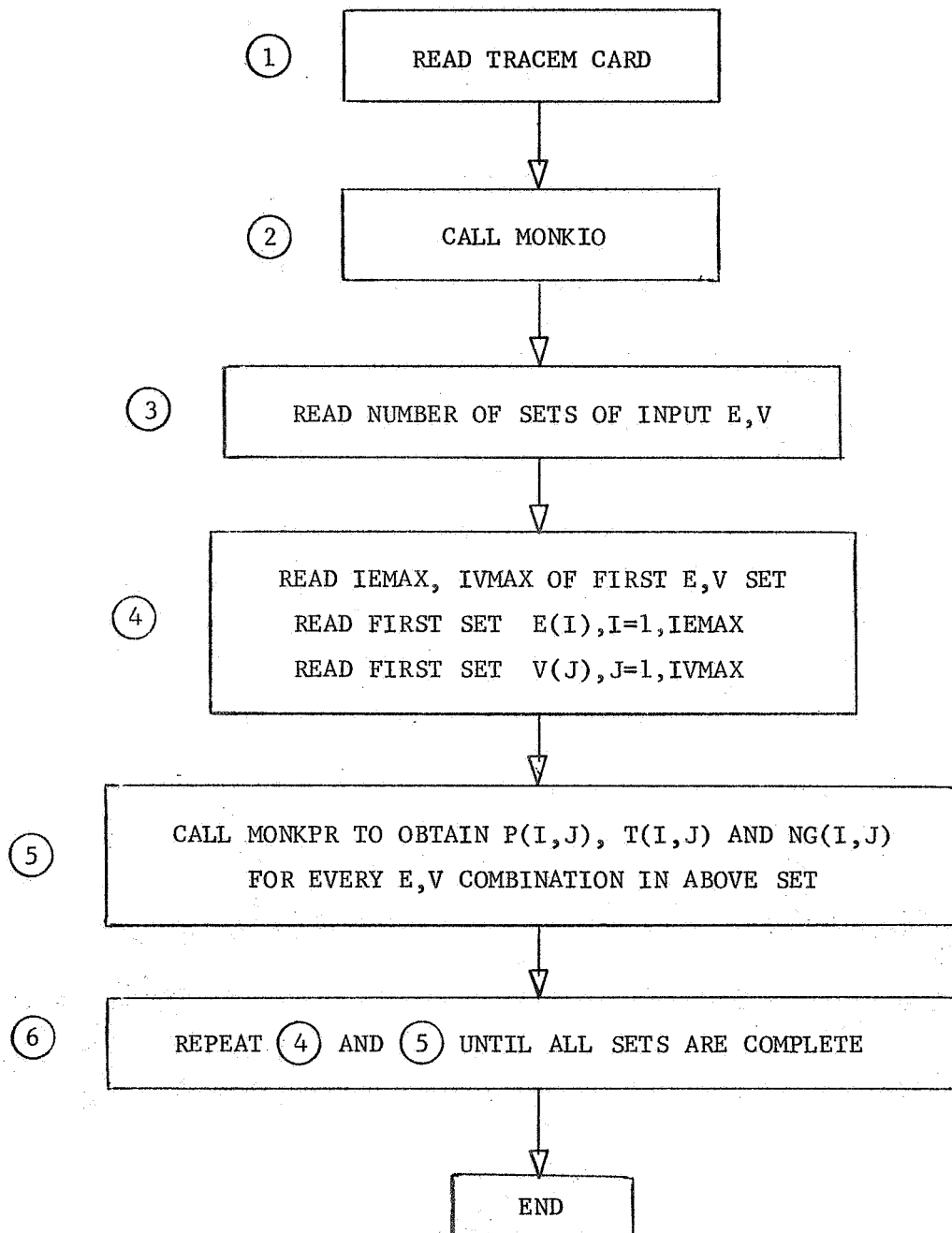
$$REV = Re/V = \frac{2\gamma r}{V} \left(\frac{n}{2\beta T} \right) \log \cosh \left(\frac{2\beta T}{n} \right) + \frac{(1-\gamma)}{V} n \tanh \left(\frac{2\beta T}{n} \right)$$

MONK NO.	NAME	(ARGUMENT LIST) /PURPOSE
39	TSUBBS	(V) /Finds sublimation temp for the given V such that $FS(V,TSUB) = FG(V,TSUB)$. A flow chart is provided elsewhere.
40	TESBNS	(V,E) /Finds temperature of solid consistent with given V and E.
41	VPSPGB	(V,T,VO,NG) /Finds volume of gas in a mixed phase case such that the gas pressure is equal to the solid pressure.
42	TEGBNS	(V,E) /finds gas temperature given V and E
43	VCRGET	(TCRIT,VCRIT,VCNT,TSUBL,VSUBL) /(1) Finds VCRIT if VCRIT is not inputted. (2) Finds index VCNT = J of VSUBL(J) and TSUBL(J) such that $TSUBL(J-1) < TCRIT < TSUBL(J)$
44	FALPHA	(T) /Returns $\alpha(T)$ = thermal coeff. of volume expansion by interpolation of input ALPHA, TEMP tables.

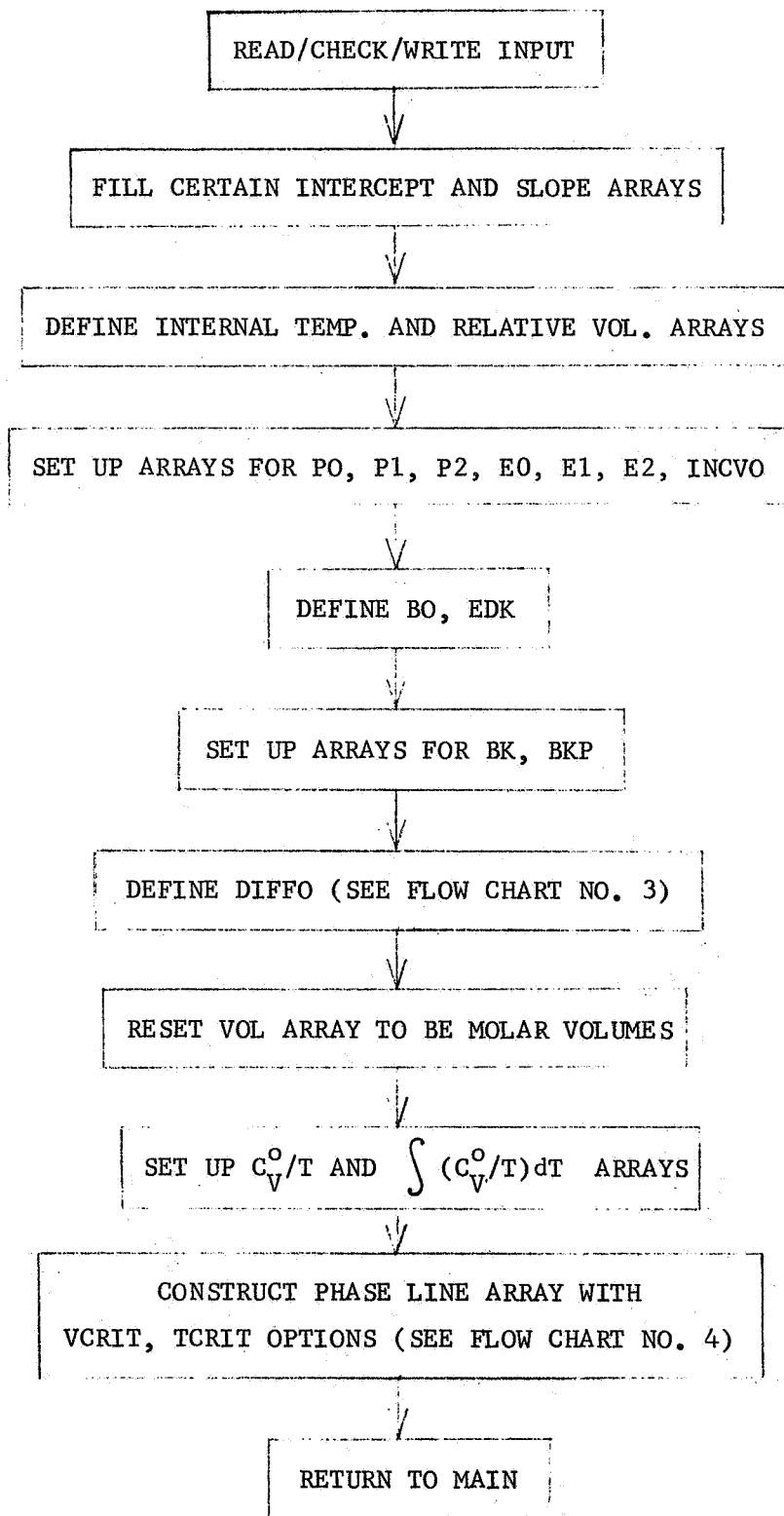
MONK NO.	NAME	(ARGUMENT LIST) /PURPOSE
45	FCVO	(T) /Returns $C_v^O(T)$ for a given T
46	FCVODT	(T) /Returns $CV(T)/T$ for a given T
47	WHEREM	(SPN,INOUT) /Computes and writes out "leaving" and "entering" and nesting level of calls to subprograms with number SPN, activated by TRACEM(SPN) \neq 0 on input card.
48	WHATMR	(SPN,N,NM1,VL1,NM2,VL2,NM3,VL3,NM4,VL4) /Writes out relevant floating point data that was generated by the subroutine that calls it if TRACEM(SPN) \neq 0.
49	WHATMI	(SPN,N,NM1,VL1,NM2,NM3,VL3,NM4,VL4) /Same as WHATMR except fixed point data.
51	DUMPEM	(SPN,N,A,NAME) /Writes out array A (of any length). Similar to WHATMR, except WHATMR writes out four arrays in four parallel columns.

MONK NO.	NAME	(ARGUMENT LIST)	/PURPOSE
52	REDFGN	(N,X,Y,NAMEX1,NAMEX2,NAMEY1,NAMEY2,LOVALX,HIVALX,LOVALY,HIVALY)	/Reads in two arrays, names and limits.
53	MONKIO	/The controlling subroutine for setting up intermediate tables and useful variables. A flow chart is provided elsewhere.	
54	MONKPR	(V,E,T,P,NG)	/After MONKIO has set up the intermediate tables and variables, MONKOO sends input pairs of V,E to MONKPR for processing to obtain P,T, and NG. A flow chart is provided elsewhere.

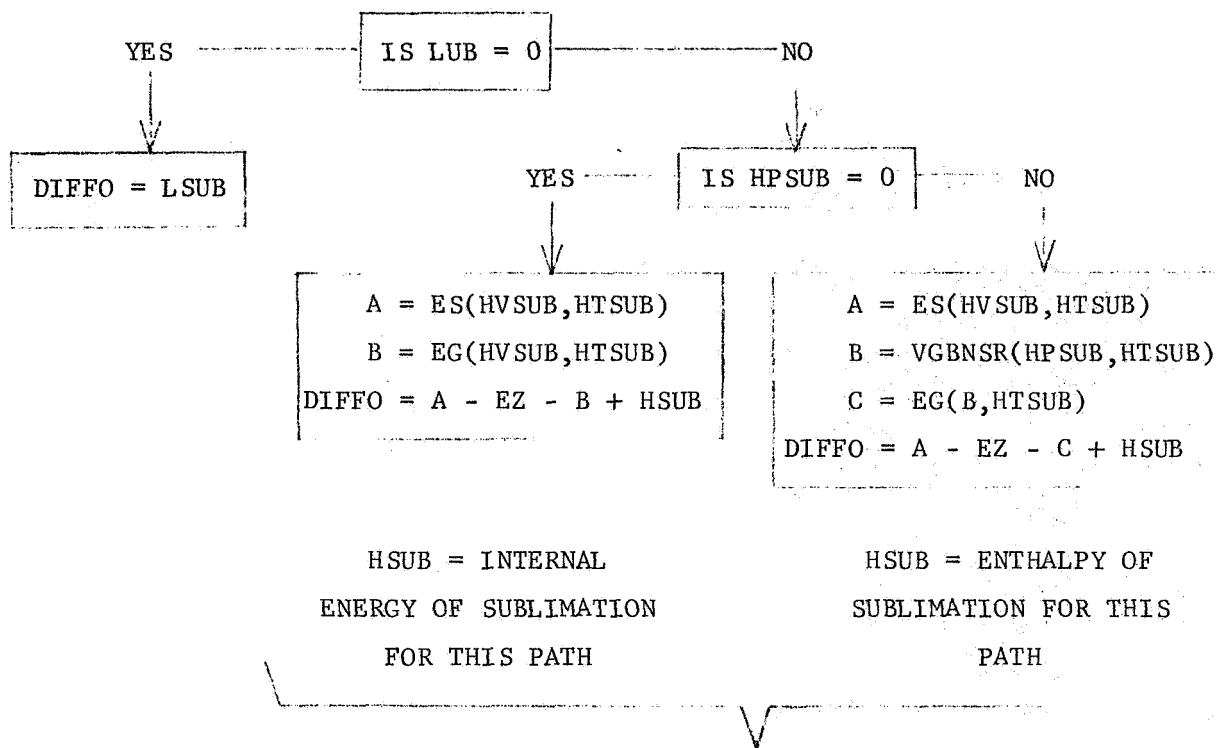
MONK MAIN FLOW CHART NO. 1



MONKIO FLOW CHART NO. 2



MONKIO-DIFFO LOGIC, FLOW CHART NO. 3

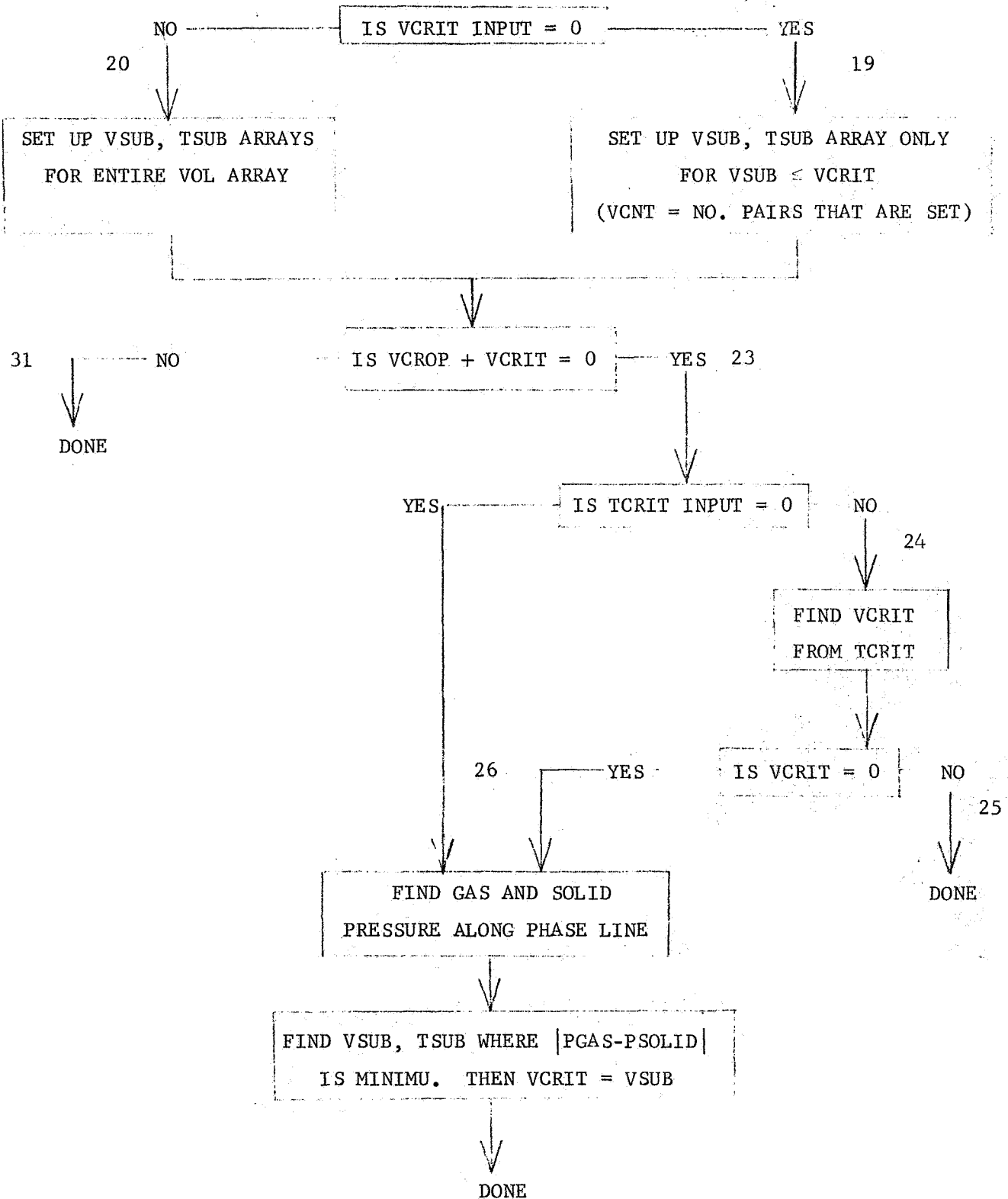


(HVSUB, HTSUB) ARE A (VOL, TEMP) PAIR
AT A KNOWN SUBLIMATION POINT

IF HPSUB IS GIVEN, THEN HSUB MUST CORRESPOND
TO THE ENTHALPY OF SUBLIMATION

IF HPSUB = 0, THEN HSUB MUST CORRESPOND TO
THE INTERNAL ENERGY OF SUBLIMATION

MONKIO VCRIT, TCRIT LOGIC, FLOW CHART NO. 4



MONKPR FLOW CHART NO. 5

